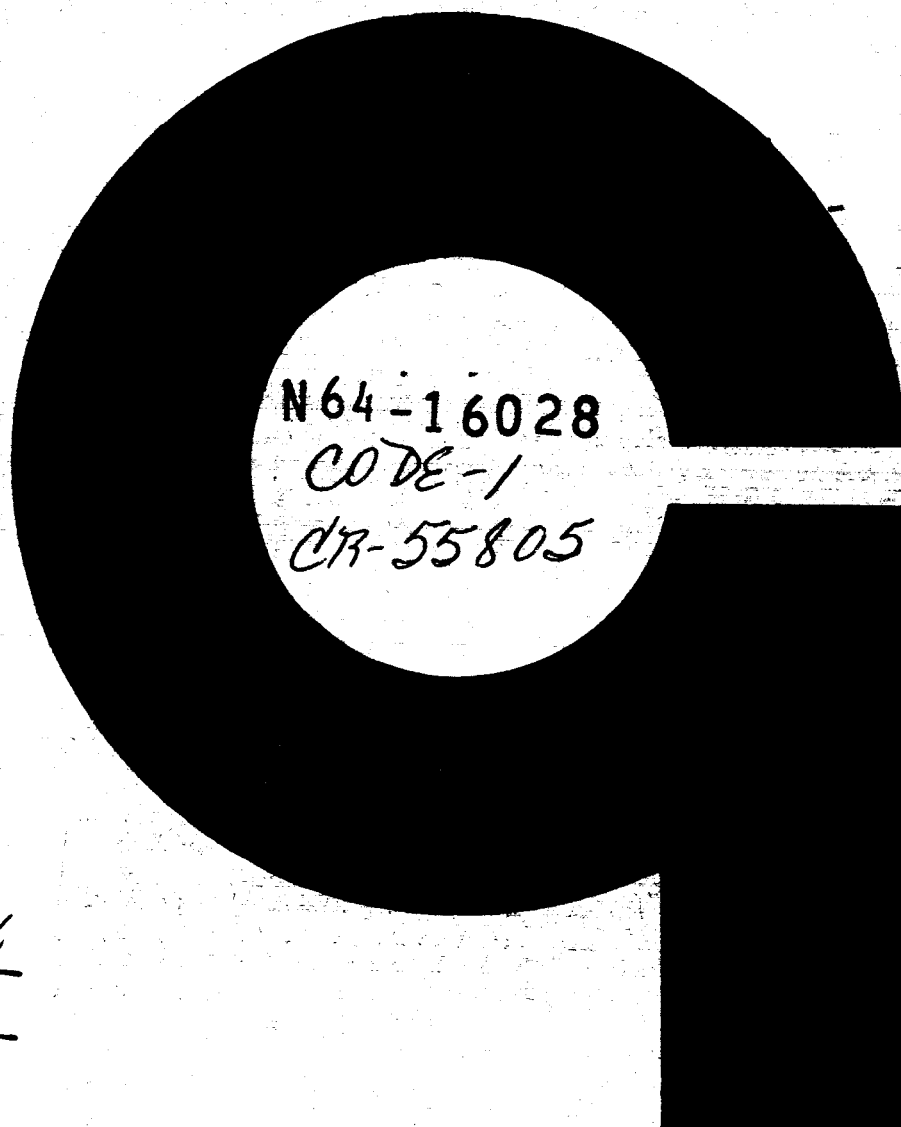


32p.



OTS PRICE

XEROX \$ 3.60 ph
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PLANETARY PHYSICS II:
LABORATORY STUDIES OF THE CHEMILUMINESCENCE
FROM THE ATOMIC OXYGEN-NITRIC OXIDE REACTION
UNDER UPPER ATMOSPHERIC CONDITIONS

N. Jonathan and G. Doherty

CONTRACT NO. NASw - 840

PREPARED FOR
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
HEADQUARTERS
WASHINGTON, D. C. 20546

JANUARY 1964

GEOPHYSICS CORPORATION OF AMERICA BEDFORD, MASSACHUSETTS

(NASA CR - - - ; ^{- TR -} GCA Technical Report No. 64-2-N } OTS.

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(NASA Contract No. NASw-840

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GEOPHYSICS CORPORATION OF AMERICA
Bedford, Massachusetts 01730

Submitted for publication in Discussions of Faraday Society.
To be presented at Faraday Society Meeting, Edinburgh, Scotland,
April 2-3, 1964.

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N. Jonathan and G. Doherty

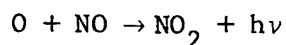
I. INTRODUCTION

The investigations of the continuum in the night airglow have been under way for many years. In early studies, Rayleigh demonstrated that its spectral distribution could not be the result of scattered sunlight.⁽¹⁾ Recent theories have independently suggested that the continuum is the result of the chemiluminescence associated with the nitric oxide-atomic oxygen reaction.⁽²⁻⁵⁾ The most recent studies of the nocturnal continuum distribution have been made by Shefov⁽⁶⁾ and Yarin⁽⁷⁾ and these workers have shown that its distribution is close to that of a laboratory-produced airglow.

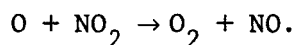
Atomic oxygen is formed above 70 km by photodissociation of oxygen molecules. Recent calculations by Wallace⁽⁸⁾ give estimates of the nighttime densities which vary from approximately 10^{10} atoms/cc at 70 km to 10^{12} atoms/cc at 100 km for a 12-hour day followed by a 12-hour night. The amount of nitric oxide present is unknown, though theoretical arguments have been put forward for its existence.⁽⁹⁾ An upper limit of 10^8 molecules/cc has been placed as a result of rocket experiments of the ultraviolet absorption spectra.⁽¹⁰⁾

Studies of the precise altitude of the continuum have been hampered by the low light intensity levels but rocket experiments have suggested

that the strongest emission lies between 90 and 110 km.^(11,12) The essential mechanism for the nitric oxide-atomic oxygen light emission is



followed by the fast reaction



Extensive laboratory studies have been made of this reaction in the pressure range 1-5 mm Hg. Most recent experiments have indicated that in the 1 mm pressure range the chemiluminescence is the result of a three-body reaction although the light emission is second order, dependent only on atomic oxygen and nitric oxide concentrations.⁽¹³⁻¹⁵⁾ The rate constant for light emission has been measured in the classic experiment of Fontijn and Schiff and found to be 1.7×10^{-17} cc molecule⁻¹ sec⁻¹.⁽¹⁶⁾ However, these workers cast doubt upon the applicability of their value under upper atmospheric pressure conditions since it was believed the chemiluminescence would become pressure dependent below 10 microns. The present study was, therefore, undertaken to extend laboratory measurements to pressure regions similar to those which exist in the region of the airglow. The experimental data may then be used to calculate whether there is sufficient atomic oxygen and nitric oxide present in the atmosphere to produce the observed night airglow continuum.

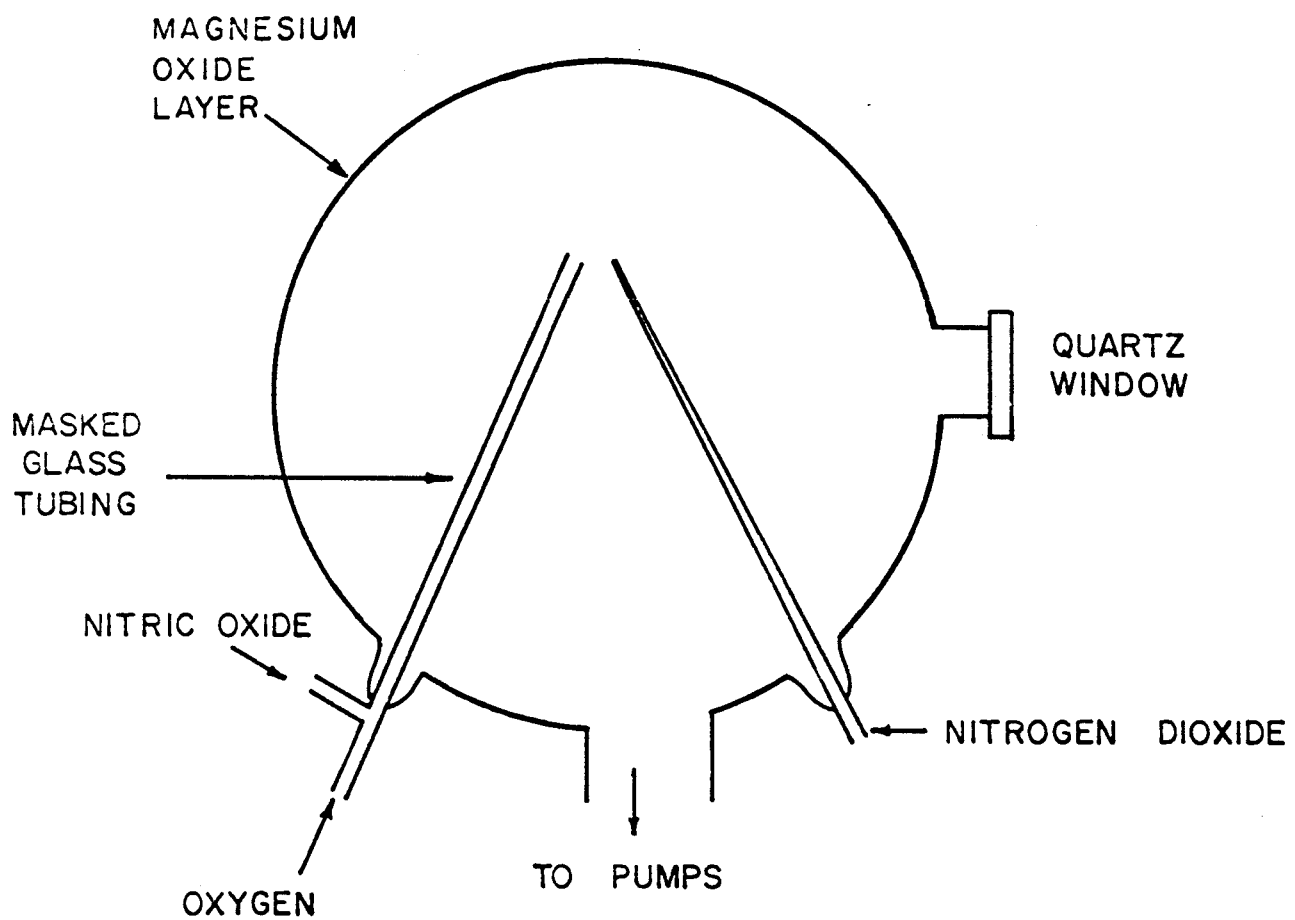


Figure 1. Reaction cell for observation of chemiluminescence.

II. EXPERIMENTAL

The reaction cell used in the present studies has been developed along the lines of multipath cells which are common in absorption spectroscopy. The light emitted during a relatively slow reaction such as $\text{NO} + \text{O}$ does not approximate to a point source and hence one must use a multi-reflection reaction cell in order to gather maximum light. The cell is shown in schematic form in Figure 1. It consists of a 50-liter, 3-necked Pyrex flask. The gases are let into the cell through the two side arms or are mixed at the point of entry in one side arm. The center arm is connected to an N.R.C. oil diffusion pump backed by a large Welch mechanical pump which, working together, are capable of maintaining the cell pressure at 3 microns Hg when the input flow is 26 standard cc's/minute. The outside of the cell is coated with a layer of magnesium oxide which gives up to 97% reflectivity. Magnesium oxide, being a diffuse reflector, has an advantage in this case over the conventional reflector in that each reflection increases the light-gathering power of the cell. The light emerges through a small aperture in the side of the cell which is sealed with a quartz window. Provided that this aperture is small, the light which is emitted can be made to approximate to a point source. This allows a maximum amount of light to be focussed through the spectrometer or on a photomultiplier. Provision is made for the cell to be heated to a maximum of 700°K by means of an external heating jacket fitted over the cell. Uniform heating of the cell is thus ensured and the temperature is controlled by varying the voltage

applied to the heating circuit. The temperature within the cell is measured by means of a calibrated thermocouple wire which enters the cell through one of the side arms. The cell pressure is measured by means of two independently calibrated McLeod gauges which are also inserted through a side arm.

A block diagram of the apparatus used is shown in Figure 2. Molecular oxygen or a mixture of molecular oxygen and inert gas is passed--via a flowmeter, needle valve and trap--through a microwave discharge unit. The partially dissociated molecular oxygen then enters the reaction vessel after first passing through the Wood's light trap. Nitric oxide which has been purified by passage through a column of ascarite (to remove NO_2) is mixed with the oxygen at the point of entry into the reaction vessel after first passing through a needle valve, a calibrated flowmeter and a dry ice-acetone trap (on the low-pressure side of the needle valve) to remove any last traces of impurities.

All flowmeters used during the program were calibrated directly on the system for all gases which passed through them, using the apparatus which is shown in block diagram form in Figure 3. The flow path of the gas is self-explanatory, the volume which passed through the flowmeter being measured at atmospheric pressure which avoided the necessity for correcting the results for the pressure at which the flowmeters were operating.

The steady-state concentration of oxygen atoms in the reaction vessel was measured at the end of each set of readings by titration

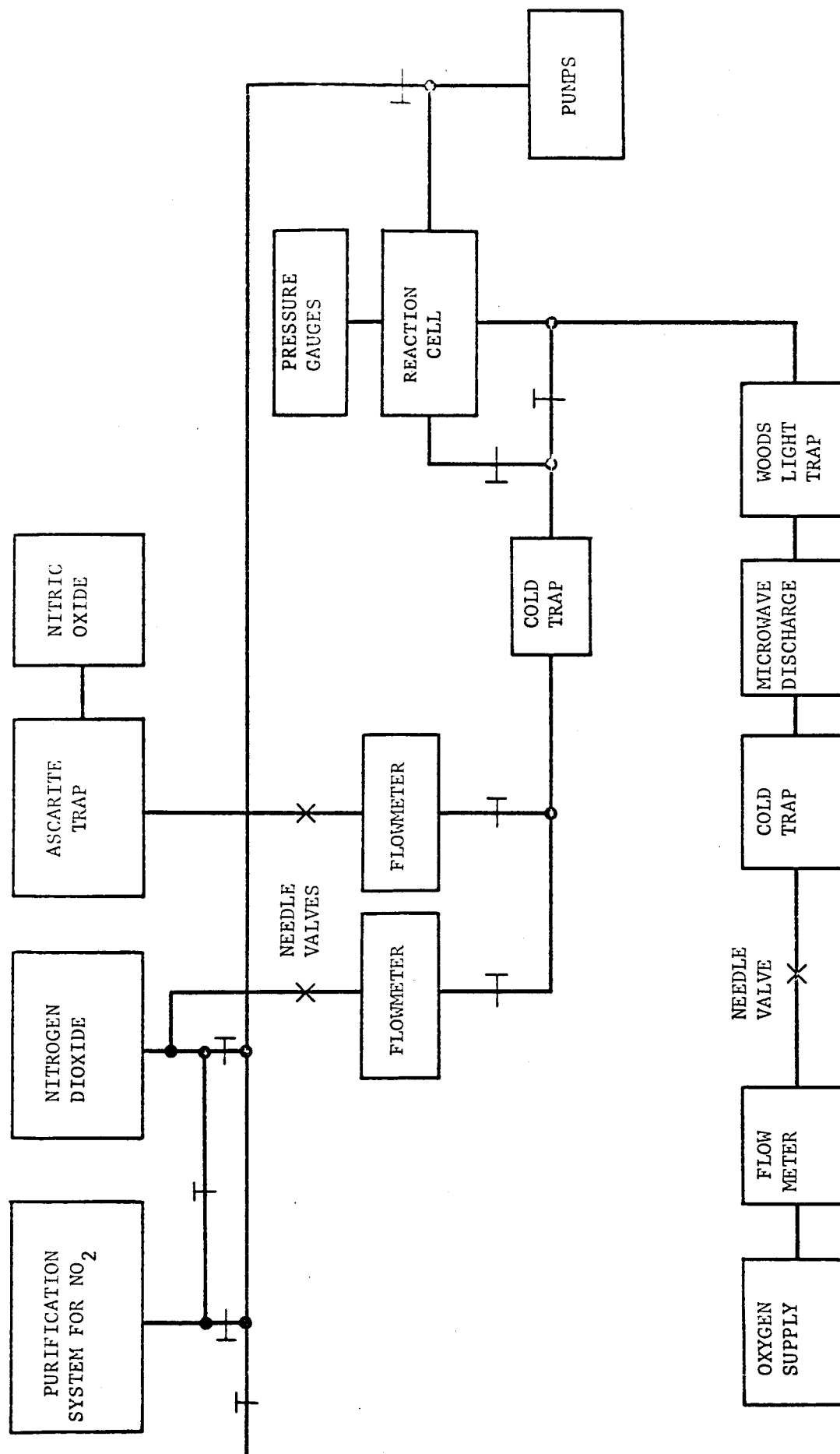


Figure 2. Block diagram of complete apparatus for observation of chemiluminescence.

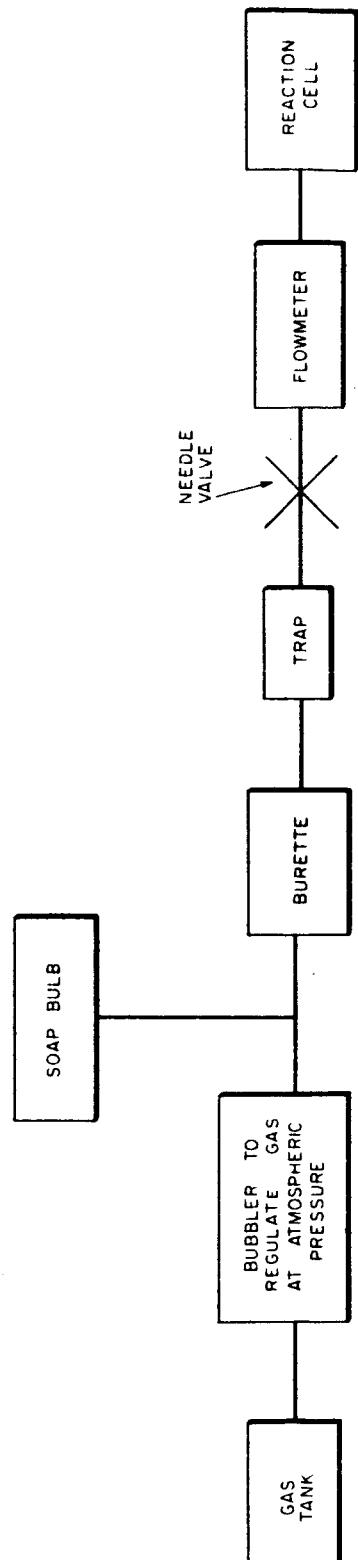
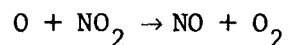
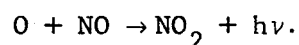


Figure 3. Block Diagram of Apparatus for Calibration of Capillary Flowmeters.

with nitrogen dioxide. The well-known reaction goes according to the equation



which is very much faster than the light emitting reaction



It can readily be seen that maximum light emission will occur when the nitrogen dioxide concentration is equal to one-half that of the oxygen atom concentration. A crosscheck on the purity of the nitric oxide and the accuracy of the titration technique was obtained from the fact that in all cases the maximum intensity from the titration was equal to the light emission when the nitric oxide partial pressure was one quarter that of the oxygen atoms. Two methods were used to observe the light emission from the nitric oxide-atomic oxygen reaction.

The spectral distribution of the light emission was obtained using a Perkin-Elmer 112 G grating spectrometer equipped with a single beam, double pass monochromator. Attempts were made to record the spectrum between 3000 and 7000 Å. Above 3200 Å, a Pyrex filter was inserted in order to avoid the presence of higher orders from the grating. The radiation passing through the monochromator was chopped on its second pass using a chopping frequency of 13 cps. This avoided the detection of the unchopped first-pass radiation since the resulting signal was fed into an amplifier tuned to the chopping frequency. The light was detected at the exit slit of the monochromator by an EMI 9558B

tri-alkali photomultiplier tube which was mounted in a light-tight housing. The spectral region was scanned automatically.

The over-all light emission was measured by mounting an RCA 1P28 photomultiplier tube, in a light-tight housing, directly onto the aperture of the reaction cell. The resulting DC signal was fed into a Victoreen microammeter. Checks were made to ensure that the photomultiplier and microammeter gave linear readings over the range of light emission encountered.

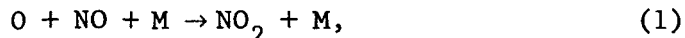
III. RESULTS

A. THE SPECTRUM OF THE LIGHT EMISSION

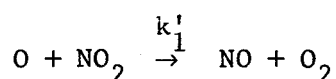
The spectrum of the chemiluminescence was obtained between 3500 and 7500 Å at pressures of 100 μ and 400 μ . Under our conditions of low resolution, the spectrum appeared as the usual airglow "continuum" with a maximum intensity at approximately 6500 Å. The light emission at pressures below 100 μ was too low to enable spectroscopic measurements. However, very crude measurements of light yields were made in various spectral regions from 3500 to 7500 Å using a 1P28 photomultiplier (S 13 cathode) and an EMI 9558B photomultiplier (S 20 cathode) in conjunction with Corning short wavelength cut-off filters at 5500 and 6300 Å. By comparison of the readings obtained with and without the filters present at 10 μ and at 100 μ , it was indicated that there was no obvious change in the spectral distribution at the lower pressure.

B. DEPENDENCE OF THE LIGHT EMISSION ON CHANGES IN CONCENTRATION OF SPECIES AND VARIATION OF THE PRESSURE.

The atomic and molecular oxygen partial pressures were maintained at constant values with an oxygen flow rate of 26 cc/min before partial dissociation. Small amounts of nitric oxide were added, via a calibrated flowmeter, to the oxygen stream at the point of entry into the reaction vessel. Below 30 microns there was virtually no loss in atomic oxygen during the residence time in the reaction vessel. At pressures above this, there were losses as a result of the three-body recombination reaction



which has a rate constant of approximately $6.0 \times 10^{-32} \text{ cc}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$. (13,17,18,19) The partial pressure of nitric oxide remained unchanged since the amount used up in forming nitrogen dioxide was regenerated immediately by the very fast secondary reaction



where $k'_1 = 2.6 \pm 0.6 \times 10^{-12} \text{ cc molecule}^{-1} \text{ sec}^{-1}$.

Hence, according to reactor theory, the difference between initial and steady-state concentrations of atomic oxygen at any pressure was

$$\frac{(\text{O}_0 - \text{O})}{t} = 2k_1(\text{O})(\text{NO})(\text{M})$$

where O_0 and O were the initial and steady-state concentrations of atomic oxygen respectively; and where (NO) was the initial (and steady state) concentration of nitric oxide, (M) was the total concentration. All these concentrations were expressed in units of molecules (or atoms)/cc. The residence time t of the species in the reaction vessel was equal to V/F where V was the volume in standard cc's and F was the total flow-rate in standard cc's/sec. Hence, in Table 1 it was calculated that at a total pressure of 43.5 microns, with a nitric oxide partial pressure of 2 microns and a residence time of 6.6 seconds, there was a 7% loss in the atomic oxygen concentration. At higher pressures the corrections became more severe and difficult to apply.

The pressure in the reaction cell was varied from 3 to 200 microns by closing the valve between the pump and the cell. At the

Table 1

Intensity as a Function of the Atomic Oxygen and Nitric Oxide Partial Pressures
over a Total Pressure Range of 3 to 200 microns*

Run No.	Total Pressure (microns Hg)	Atomic Oxygen Pressure (microns Hg)	Nitric Oxide Concentration (microns Hg)	Intensity ($\times 10^6$ amps)	Intensity	
					per micron Nitric Oxide ($\times 10^6$ amps)	I_0 ($\times 10^5$ amps)
1	3.0	0.13	0.36	.297	0.825	0.63
2	9.5	0.44	0.90	2.07	2.3	0.52
3	19.5	0.90	2.1	10.8	5.14	0.57
4	30.0	1.35	3.3	25.8	7.82	0.58
5	43.5	1.93	2.0	21.0	10.5	0.54
	43.5	(1.79) [†]	2.0			0.59 [†]
6	80.0	3.38	1.0	14.7	14.7	0.49
		(3.01) [†]				
	80.0	3.38	2.0	28.7	14.35	0.53 [†]
		(2.70) [†]				
	80.0	3.38	3.0	39.0	13.0	0.53 [†]
		(2.43) [†]				
6(b)	80.0	1.69	1.69	14.0	8.28	0.59 [†]
		(1.40) [†]				
7	200.0	4.33	4.33	26.0	6.0	0.64 [†]
		(0.94) [†]				

* Intensities are taken from straight line plots as illustrated in Figure 4, except for Runs 6(b) and 7 where the peak intensity of the titration with NO₂, as observed by the photomultiplier under identical conditions, is used.

† These values are corrected for loss of atomic oxygen by three-body recombination, as explained in the text.

end of each series of additions of nitric oxide, the atomic oxygen flow-rate was measured by titration with nitrogen dioxide and the resultant light emission was plotted as a function of NO_2 flow rate. Hence, knowing the flowrates of molecular oxygen, atomic oxygen and nitric oxide, and the total pressure, the partial pressure of each constituent was calculated. The light emission was plotted as a function of the nitric oxide partial pressure at each different total pressure. Below 40 microns, straight line plots were obtained but above this point a slight curvature appeared which became severe at 80 microns and higher. This, as already explained, was due to losses in the atomic oxygen partial pressure as a result of the three-body non-radiative recombination process. The results of a typical low-pressure run are given in Figure 4. It may be seen that the light emission is directly proportional to the nitric oxide partial pressure. If one defines I_0 as the light emission per micron of nitric oxide and atomic oxygen such that

$$\text{Intensity} = I_0 [\text{O}][\text{NO}] ,$$

then an essentially constant value is obtained for I_0 . The results of the runs over the pressure range 3 to 200 microns are given in Table 1 and Figure 5. It may be seen from Table 2 that the light emission is directly proportional to the atomic oxygen and nitric oxide partial pressures and independent of the total pressure (and hence third body) over the range 3 to 80 microns and seemingly as high as 200 microns. However, this last result--although agreeing with theory--must be treated with caution owing to the severity of the correction which had to be applied.

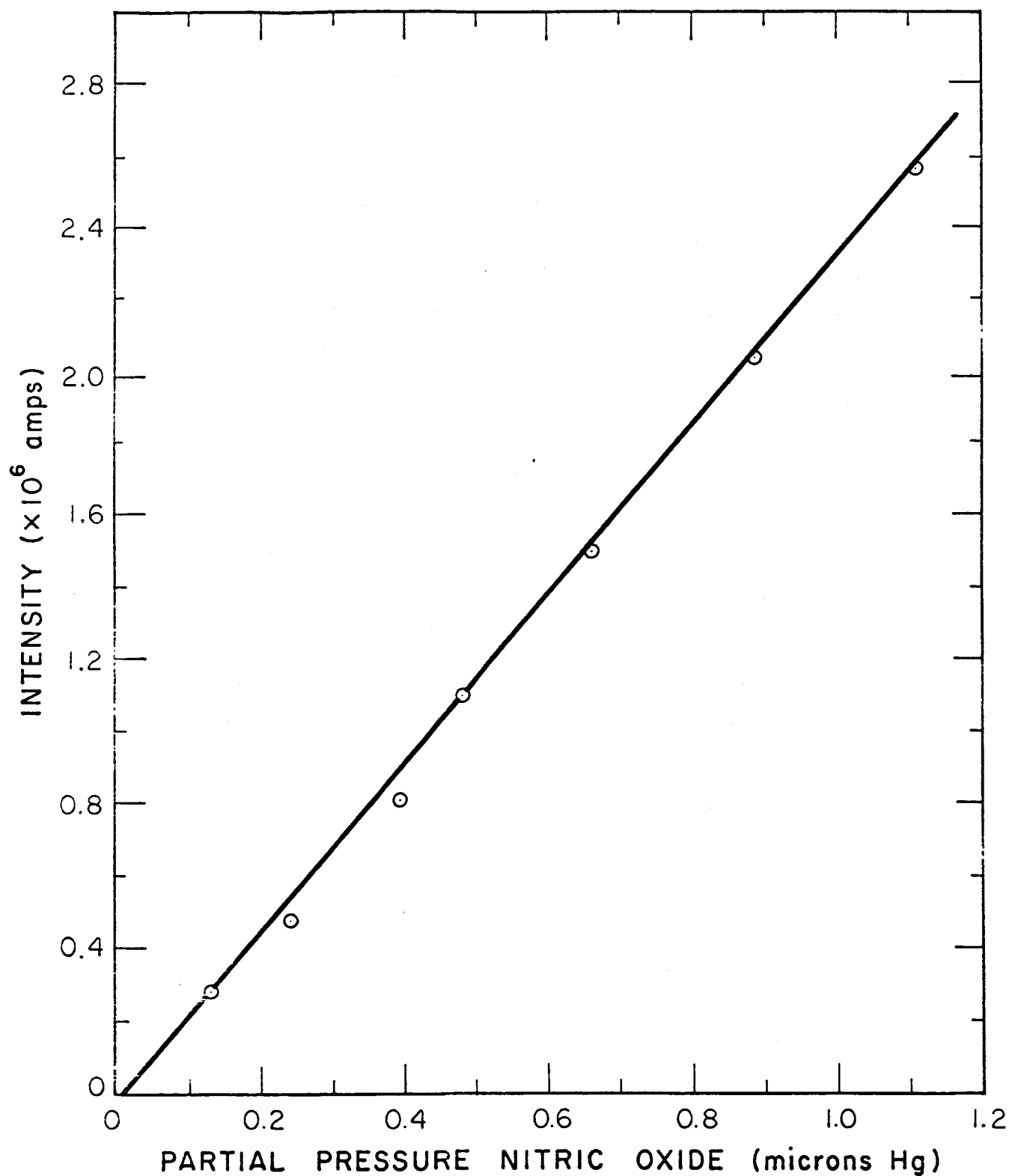


Figure 4. Light Emission as a Function of Nitric Oxide Partial Pressure at Constant Initial Pressure of 9.5 microns.

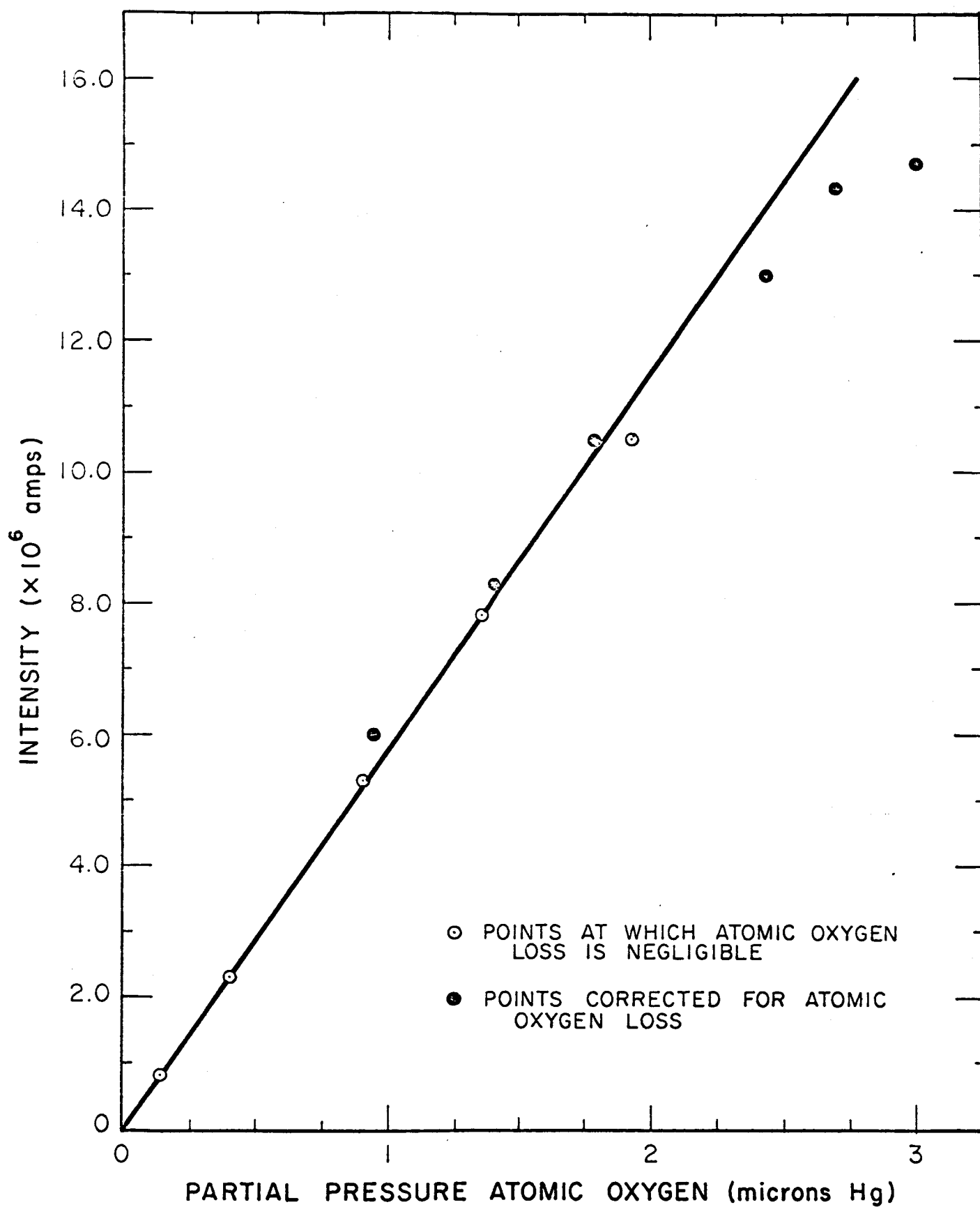


Figure 5. Light Emission as a Function of Atomic Oxygen Partial Pressure Over the Total Pressure Range 3 to 200 microns.

Table 2

Intensity as a Function of Nitric Oxide Partial Pressure at a Total Initial Pressure of 9.5 microns and Atomic Oxygen Partial Pressure of 0.44 microns

Total Pressure Before NO Addition (microns Hg)	Pressure Atomic Oxygen (microns Hg)	Pressure Nitric Oxide (microns Hg)	Intensity ($\times 10^6$ amps)	I_o ($\times 10^5$ amps)
9.5	0.44	1.11	2.58	0.53
9.5	0.44	0.89	2.04	0.52
9.5	0.44	0.66	1.50	0.52
9.5	0.44	0.48	1.11	0.53
9.5	0.44	0.39	0.81	0.47
9.5	0.44	0.24	0.48	0.45
9.5	0.44	0.13	0.29	0.51

The direct relationship between the atomic oxygen partial pressure and the light emission was further investigated under conditions of constant total pressure and a fixed partial pressure of nitric oxide. The atomic oxygen partial pressure was varied by changing the power of the microwave discharge. After each set of runs the atomic oxygen partial pressure was measured as already explained. The results are shown in Table 3 and Figure 6. It can again be seen that the light emission is directly proportional to the atomic oxygen concentration and that I_o has a constant value in good agreement with the other data.

Attempts were made to study the light emission at pressures below 3 microns by reducing the flowrate of oxygen to 9-10 cc/min. In this way the light emission was studied over the pressure range 0.85 to 7.5 microns. These results are given in Table 4. It may be seen that the value of I_o is again constant but is somewhat lower than before. However, I_o is still independent of the amount of third body present otherwise I_o would show a pressure dependence. It is easily appreciated that at these low pressures, a small error in the measurement of either pressure or flowrates may result in this I_o difference. Hence, since the constancy of I_o still holds, we attribute this lower I_o to an inherent experimental error.

C. EFFECT OF ADDED GASES

The pressure of the reaction vessel was maintained at 3, 30 and 100 microns with constant flows of atomic and molecular oxygen and nitric oxide. Small amounts of dry air, oxygen and nitrogen were added, in turn,

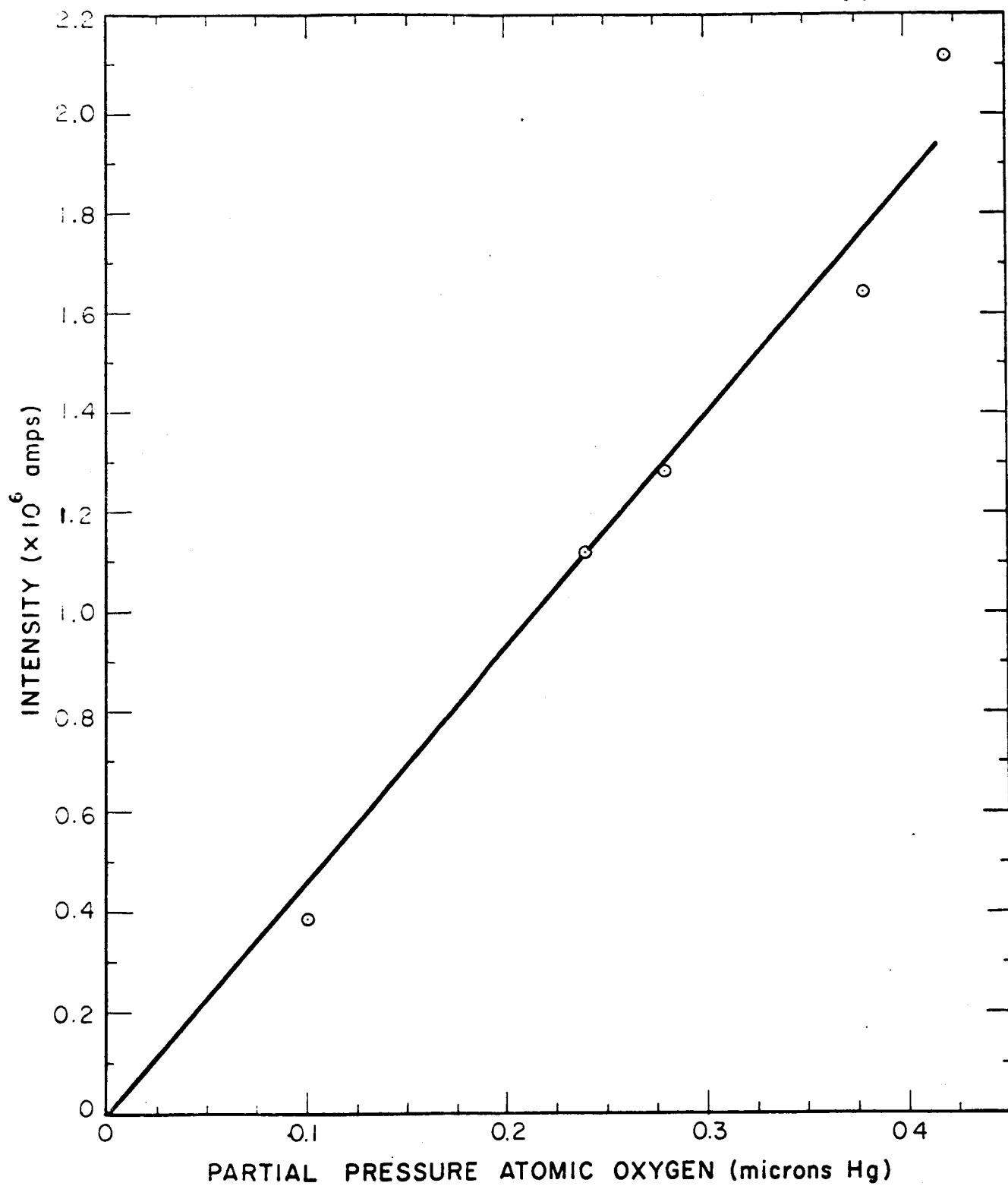


Figure 6. Light emission as a function of atomic oxygen partial pressure at a total pressure of 9.5 microns.

Table 3

Intensity as a Function of Atomic Oxygen Partial Pressure at a Total Pressure of
9.5 microns and Nitric Oxide Partial Pressure of 0.8 microns

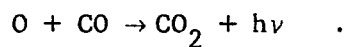
Run No.	Total Pressure Before NO Addition (microns Hg)	Pressure Atomic Oxygen (microns Hg)	Pressure Nitric Oxide (microns Hg)	Intensity ($\times 10^6$ amps)	I_o ($\times 10^5$ amps)
1	9.5	0.10	0.80	0.388	0.49
2	9.5	0.24	0.80	1.08	0.56
3	9.5	0.28	0.80	1.28	0.57
4	9.5	0.38	0.80	1.64	0.54
5	9.5	0.42	0.80	2.12	0.63

Table 4

Values of I_o at Flowrates of 9-10 cc/min

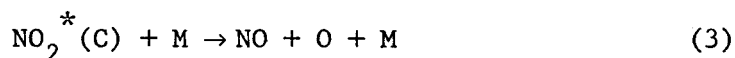
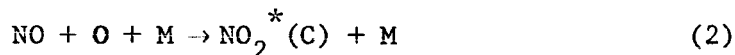
Total Pressure Before NO Addition (microns Hg)	Pressure Atomic Oxygen (microns Hg)	Pressure Nitric Oxide (microns Hg)	Intensity ($\times 10^6$ amps)	I_o ($\times 10^5$ amps)
0.85	0.044	0.2	0.037	0.42
1.0	0.065	0.2	0.052	0.40
5.0	0.234	2.0	1.80	0.38
7.5	0.442	2.0	3.30	0.37

up to amounts not exceeding 10% of the total flow. The additions gave a negligible change in the light emission indicating that there was little, if any, quenching by the added gases. Attempts were made to make similar experiments with carbon monoxide as the added gas, but these results showed a slight but definite increase in the light emission which was probably a result of the chemiluminescent reaction



IV. DISCUSSION

It is felt that our experimental data are in full agreement with the three-body mechanism already postulated for the reaction.⁽¹⁴⁾ In order to facilitate comparison between the original derivation of this mechanism and its description here, the original equation numbers, etc., are maintained. It has been suggested that two excited states of NO₂ are formed during the reaction. These are written as NO₂^{*}(B) and NO₂^{*}(C).



Neglecting emission from the NO₂^{*}(C) state owing to its longer lifetime,⁽²⁰⁾ the steady-state treatment for light emission yields

$$I = \frac{k_2 k_4 k_{6B} [\text{NO}][\text{O}][\text{M}]}{(k_3 [\text{M}] + k_{7C} [\text{M}]) (k_{7B} [\text{M}] + k_5 + k_{6B}) + k_4 (k_{7B} [\text{M}] + k_{6B})} \quad (8)$$

At pressures of 1 mm or less, the equation is further simplified by assuming collisional deactivation to be an efficient process with nearly every collision effective. k_{6B} is given as $4 \times 10^6 \text{ sec}^{-1}$ (20)

and $k_{7B}[M]$ and $k_{7C}[M]$ are approximately $1 \times 10^6 \text{ sec}^{-1}$ at 300 microns.

Hence, simplifying where $k_{6B} \gg k_{7B}[M]$

$$I = \frac{k_2 k_4 k_{6B} [NO][O][M]}{(k_3[M] + k_{7C}[M])(k_5 + k_{6B}) + k_4 k_{6B}}, \quad (9)$$

At low pressure $k_{6B} \gg (k_3[M] + k_{7C}[M])$ and since I is independent of pressure, then $k_4 \ll (k_3[M] + k_{7C}[M])$ which means also that $k_{6B} \gg k_5$.

Hence,

$$I = \frac{k_2 k_4 [NO][O][M]}{(k_3[M] + k_{7C}[M])} \quad (10)$$

This equation is then in agreement with the observed pressure independence of the light emission in spite of the three-body process. It is also consistent with the difference in the third-body efficiency as found by Clyne and Thrush⁽¹⁵⁾ since $k_{7C}[M]$ varies according to the nature of M . It has been pointed out by Fontijn and Schiff that this pressure independence must be lost at sufficiently low pressures since $(k_3 + k_{7C})[M] \gg k_4$ will not hold. Inserting the suggested reasonable values of $k_3 \approx 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $k_{7C} \approx 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, we find that at 1 micron total pressure k_4 must be considerably less than $6.6 \times 10^3 \text{ sec}^{-1}$ for the light emission to remain pressure independent. In view of our results it is therefore suggested that a more reasonable maximum value for k_4 is 10^3 sec^{-1} rather than the suggested 10^4 sec^{-1} , which does not conflict with the above mechanism and

is consistent with the experimental results. It may also be noted that our observation, indicating there was virtually no quenching by added gases, is consistent with this mechanism.

An alternative mechanism would be the direct two-body recombination reaction



Provided that k_{13} is negligible, then the light emission would again be independent of pressure. In this case, however, one cannot explain the different third-body efficiencies found by Clyne and Thrush. Hence, although on first thought it may possibly seem unreasonable to speak of a three-body mechanism at pressures as low as 1 micron, we feel that all the experimental data make it necessary to do so in this case.

The results indicate that the value previously obtained for the rate constant for light emission of $1.7 \times 10^{-17} \text{ cc molecule}^{-1} \text{ sec}^{-1}$ (16) is applicable down to pressures of 0.85 microns which corresponds to an altitude of 93.5 km. (21) This rate constant was therefore used to calculate the possible photon flux of the nighttime airglow continuum using the formula

$$\frac{[\text{NO}_2^*]}{dt} = 1.7 \times 10^{-17} [\text{O}][\text{NO}] \quad .$$

The values for the oxygen atom concentrations are taken from the recent calculations by Wallace for a 12-hour day and night cycle. ⁽⁸⁾ The nitric oxide concentration is given the allowed upper limit value of 10^8 molecules/cc. ⁽¹⁰⁾ The results are given in Table 5. The total photon flux is calculated as approximately 3×10^9 photons/cm²/sec. The field data obtained by Shefov ⁽⁶⁾ indicate a total integrated emission of approximately 3300 Rayleighs in the spectral region between 3900 and 6200 Å. This corresponds to a total flux of 3.3×10^9 photons/cm²/sec, which is in agreement with our calculated data but no great accuracy is to be expected or claimed when one considers the uncertainty in the nitric oxide concentration distribution. It is perhaps trivial to point out that the derived distribution of photons over the range 70-110 km is in apparent agreement with the distribution of the airglow continuum as measured by rocket experiments. This must obviously be the case since the atomic oxygen concentration follows this distribution and a uniform concentration of nitric oxide has been assumed.

Table 5

Possible Photon Flux from the Night Airglow Continuum Assuming the Cause
to be the $O + NO$ Reaction

Altitude (km)	Total Particle Concentration (molecules/cc)	Atomic Oxygen Concentration (atoms/cc)	Nitric Oxide Concentration (molecules/cc)	Flux (photons/cm ² /sec)
70	2.1×10^{15}	1×10^{10}	10^8 }	26×10^6
80	4.0×10^{14}	2×10^{10}	10^8 }	1×10^8
90	5.9×10^{13}	1×10^{11}	10^8 }	1×10^9
100	7.8×10^{12}	1×10^{12}	10^8 }	1.7×10^9
110	1.2×10^{12}	1×10^{12}	10^8 }	

V. CONCLUSIONS

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The following main conclusions are derived from the present work: *9.4.*

(1) The atomic oxygen-nitric oxide reaction is a three-body process down to pressures of at least 1 micron.

(2) The light emitting reaction is not pressure dependent and hence the existing rate constant for light emission of 1.7×10^{-17} cc molecule⁻¹ sec⁻¹ may be applied at total pressures as low as 1 micron.

(3) Provided that nitric oxide is present in concentrations of 10^8 molecules/cc over the altitude range 80-110 km, there should be sufficient light emitted to make the atomic oxygen-nitric oxide reaction a prime contributor to the nighttime airglow continuum.

AUTHOR

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